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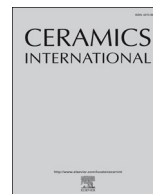
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A zeta potential and rheology study using electroacoustic spectroscopy on aqueous boron carbide suspensions

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ABSTRACT

The zeta (ζ) potential of moderately concentrated (at 15 vol%) boron carbide (B_4C) suspensions were characterised using electroacoustic spectroscopy. This technique has been validated for use in this application by correlating the ζ -potential to the suspension viscosity (at 30 vol%) across a range of pH values. Zeta potential has been shown to be effective in determining differences in B_4C powders, reported to be nominally of the same specification in terms of particle size distribution and X-ray diffraction data. The isoelectric (IEP) points for three different as-received B_4C powders were found to be 4, 7 and less than 2.5. The study showed that differences in ζ -potential across the powders can be minimised via heat treatment, which produced suspensions all with an IEP below 2.5. The study also established the effect of an anionic and a cationic dispersant on ζ -potential and rheology, demonstrating that excess dispersant from a ζ -potential perspective was required to obtain the lowest viscosity. The study concluded that as-received B_4C powders most likely contain contaminants of a cationic nature and that electroacoustic spectroscopy is a useful tool in determining their behaviour in aqueous suspensions.

1. Introduction

Boron carbide (B_4C) owes to its suitability as a material for armour, abrasives and cutting tools to its impressive mechanical and thermal properties which include ultra-high hardness, high strength, low specific gravity (2.52) and high melting point (2450 °C) [1,2]. It also acts as a neutron absorber when present as ^{10}B , which has seen its use surface in nuclear applications, and is extremely resistant to chemical attack which further extends its suitability. Yet uptake of B_4C in these areas has been severely limited due to the high costs associated with production and the unpredictability of the final component. Currently, B_4C components can be manufactured using hot pressing, hot isostatic pressing, cold isostatic pressing, tape casting, gel casting and slip casting, of which their advantages and disadvantages have been discussed at length across various literature [3–10]. This paper focuses on determining the zeta (ζ) potential and rheology of aqueous B_4C suspensions which each contain powder of nominally the same specification to reveal variances in colloidal performance. Such suspensions will be present at some stage in a number of the listed manufacturing processes and this paper will lend itself to those who face processing challenges in this area.

In general, for high quality components to be produced a high

density and uniform green body must be achieved at the ceramic forming stage. Take slip casting, for example, this requires the preparation of a well dispersed suspension that is stable in the time frame of casting the desired component. The viscosity of the suspension must also remain low ($< 1 \text{ Pa s at } 10 \text{ s}^{-1}$) for the process to work effectively [11]. Conveniently, viscosity can act as an indirect measure of how well dispersed a suspension is, with lower viscosities signifying a more well dispersed suspension, assuming other factors are appropriately controlled. However, powders can demonstrate different behaviour in supposedly the same formulation, as this paper highlights, which may not present themselves until late on in a process and will require additives to steer performance back to within processing limits. A more direct approach is to look at the electrostatic repulsive forces acting on the particles through observation of the ζ -potential to predict behaviour. This would enable manufacturers to have a deeper understanding of their raw materials and implement changes to their process accordingly.

Zeta potential allows the determination of the electric charge distribution surrounding particles in a suspension. High squared values of ζ -potential correlate directly to the magnitude of electrostatic repulsion with values of ζ^2 greater than 625 mV^2 ($\zeta < -25 \text{ mV}$ or $\zeta > 25 \text{ mV}$), generally being regarded as having high colloidal stability [12]. Several

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studies have used ζ -potential data for B₄C suspensions as an aid to support their theories but no attempt has been made to directly correlate this data to rheology [6–10,13]. This is probably partly due to the limitations associated with the ζ -potential equipment available to them, with all the mentioned studies using electrophoretic measurement techniques. Currently this group of techniques can only be applied to very dilute levels (< 0.05 vol%), as they must be dilute enough to allow light to pass through the specimen to calculate particle velocity. This raises the question of whether observations made at this dilute level can be applied to more concentrated suspensions. A number of authors have performed comparative studies across different ζ -potential quantification techniques though a direct comparison of other techniques, such as dynamic light scattering, is not possible at the concentrations concerned in this work [14–16]. However, at dilute concentrations there is good agreement between different methods of measurement when $\kappa a > 100$ or $\kappa a < 1$, where κ is the Debye-Huckel parameter and a is particle size. In this instance the Smoluchowski equation is an excellent predictor of ζ -potential. For electroacoustic methods measuring more concentrated slurries (> 3 vol%) a correction factor must be applied for reasons demonstrated in O'Brien et al., Johnson et al. and Hunter [17–19].

This paper uses an electroacoustic technique, originally patented by Oja and Cannon, and later developed by O'Brien et al. for the determination of ζ -potential in concentrated suspensions and relates this to the rheological properties of B₄C suspensions [20,21]. Hunter and Greenwood have produced excellent reviews of electroacoustic technology used within this study when applied to colloids [22,23]. Meanwhile, Dukhin provides a thorough presentation of the mathematics involved in characterising colloids using ultrasound whilst debating the differences in approach of the electrokinetic sonic amplitude (ESA) and the colloidal vibration potential (CVP) methods [24].

Another issue this work begins to address is the disparity between different batches of B₄C which are observed when processing. Most techniques do not show material differences, for example XRD and PSD, but electroacoustic characterisation has shown promise in preliminary trials. No data on this aspect of B₄C behaviour has been published to the authors' knowledge at the time of writing. Previous works have considered only a singular B₄C batch and employ pre-treatment techniques to normalise the powders which can prove challenging to implement at larger scales (e.g. methanol washing). These pre-treatment processes can also add unnecessary expense, if the powder batch is already of a high quality. These different materials vary in behaviour when aqueously processed.

It could also be argued that manufacturers of the powder do not understand the impact their process changes have on the final product, as the same material data is given from batch-to-batch despite obvious behavioural differences. Understanding this behaviour will allow appropriate treatments to be devised for powders of different batches and from different manufacturers.

2. Experiment

2.1. Raw materials

Three B₄C powders obtained from H.C. Starck of HD7 grade were used in this study. The batches were nominated numbers 4969, 4895 and 4864. It is believed that these powders have been manufactured using an electric arc furnace to produce an ingot which was subsequently ground down to the presented particle size distribution (PSD). The data provided by the manufacturer for B₄C can be seen in Table 1.

Dispersants used in this study were Dispex AA4040, a salt of ammonium polyacrylate, supplied by BASF and branched polyethylenamine of M.W. 50,000–100,000 supplied by Alfa Aesar. For pH control in ζ -potential readings from a potentiometric titration, 1.0 M hydrochloric acid and 1.0 M sodium hydroxide (ACS Reagent Grade) were used, both supplied by Fisher Scientific.

Table 1

B₄C HD7 powder data as supplied by H.C. Starck.

	HD7 B ₄ C
Surface area (m ² /g)	6–9
D ₁₀ (μm)	0.2–0.4
D ₅₀ (μm)	1.0–2.0
D ₉₀ (μm)	3.0–5.0
Boron:Carbon ratio	3.8–4.0
Carbon (wt%)	min. 21.8
Nitrogen (wt%)	max. 0.7
Oxygen (wt%)	max. 1.2
Iron (wt%)	max. 0.1
Silicon (wt%)	max. 0.15
Aluminium (wt%)	max. 0.05
Other (Ca, Cr, Mg, Mn, Ni, Ti, W) (wt%)	max. 0.1

Orthoboric acid (H₃BO₃) ($> 99.5\%$) from Sigma Aldrich and graphite powder (general purpose grade) from Fisher Scientific were used to determine the effect of an excess of these species in raw powders. Both these powders were mixed with deionised water and diluted to allow for accurate titration of each into the slurry during electroacoustic characterisation.

2.2. Powder characterisation

For particle size distribution (PSD) measurements a Mastersizer 2000 (Malvern Instruments) with an MS-1 dispersion unit was used. This equipment uses laser light scattering to calculate particle size. A small amount of powder (< 0.2 g) was mixed into a paste with a surfactant (Triton X100 from Sigma Aldrich) and diluted with 5 ml of deionised water. The mixture was ultrasonicated for 2 min before being dropped into the dispersion unit.

X-ray diffraction (XRD) data was determined using a D2 phaser 2nd Generation (Bruker) coupled with Diffrac. Suite software (Bruker).

Oxygen and nitrogen content of raw powders was determined using a LECO ON836 which utilises inert gas fusion, infrared detection and thermal conductivity of the resultant gases.

Surface area of the powder was calculated from BET theory using nitrogen adsorption via a Quantachrome Nova 3200e analyser.

2.3. Preparation of aqueous suspensions

Preparation of B₄C suspensions was achieved by adding the required amount of powder to deionised water. This mixture was then mixed to break up large agglomerates using an overhead mixer and appropriate impeller overnight to allow for full wetting of the powder. Care was taken not introduce bubbles into the system, which would affect both ζ -potential and rheology readings.

2.4. Zeta potential experiments

Zeta potential measurements were made using an Acoustosizer IIs from Colloidal Dynamics. The system was calibrated using a polar calibration standard provided by Colloidal Dynamics which consisted of a solution of potassium silico tungstate (KSiW) ions. A silica reference material provided by Colloidal Dynamics was used to validate this calibration.

For this study, two types of experiment were performed using this equipment, a concentration series and a potentiometric series. For a concentration series, dispersant was slowly titrated into the system using an auto-titration system and ζ -potential recorded at the different concentrations. Each dispersant was diluted down to allow for more precise addition to the system. In the case of graphite addition, this was performed manually using a pipette as to not contaminate the piping of the auto titration system. For a potentiometric series, pH was varied between pH 2 and 12 using the 2.1 the auto-titration software provided

and the ζ -potential recorded. A stirrer speed of 200 rpm was used for the mixing vessel and a slurry flow rate corresponding to 150 rpm on the inbuilt peristaltic pump. The ultrasonic attenuation method was used in all cases, as the particle size of agglomerates tended to fall outside the range for electrokinetic sonic amplitude method ($> 10 \mu\text{m}$). This was particularly noticeable around the isoelectric point (IEP). A lognormal model was used for particle size data. At each pH, the ζ -potential was measured three times. All measurements were made at ambient room temperature of $25.0 \pm 1.0^\circ\text{C}$.

2.5. Rheological characterisation

For rheological characterisation of the suspensions at different pH values, a 0.3571 batch of 30 vol% suspension was mixed using the method described in Section 2.3. The pH of the suspension was measured before initial sampling. From then onwards the pH was adjusted using 1.0 M sodium hydroxide and 1.0 M hydrochloric acid with B_4C powder being added to keep the suspension the same solids concentration. After pH adjustment, the suspension was mixed for 30 min before the pH measured and samples taken for rheological characterisation.

Rheology of the samples was measured on a Gemini II rheometer from Malvern Instruments. A continuous shear ramp from 0.5 s^{-1} to 200 s^{-1} and back down was performed with an integration time of 2 s on a 40 mm stainless steel parallel plate geometry with a solvent trap at 20°C . The samples were subject to a pre-shear of 50 s^{-1} followed by 1 min of equilibration before each ramp. The instrument performed 3 subsequent up and down ramps during each measurement and each test was repeated three times. An average of the three runs at each shear rate was determined as the suspension viscosity.

3. Results and discussion

3.1. Powder characterisation

Table 2 shows the powder specification as measured by the techniques stated in Section 2.2. Comparing this to the data provided by the manufacturer in Table 1, it is evident that the particle size data provided by the manufacturer is slightly smaller when considering the d_{10} and d_{90} , though there is very little variation in terms of particle size between each of the batches. This suggests that the manufacturer may use particle size as a way of sorting the powders to get the desired surface area and it could also be a way of achieving a specified grade of powder. There may also be some form of particle enlargement occurring from time of manufacturing to the laboratory test.

The measured surface area for each of the three powders is variable with 4969 B_4C falling out of the stated specification of between 6 and $9 \text{ m}^2 \text{ g}^{-1}$. The oxygen and nitrogen content of all the powders positively correlate to the measured surface area, with 4864 having the lowest and 4969 having the highest. This observation suggests that these species are most likely concentrated on the surface of the powder.

Fig. 1 shows the XRD patterns for the three powders. All the peaks were identified using Diffraction Suite and correlated to either B_4C (various stoichiometry) or free carbon in the powder. Free carbon, most likely

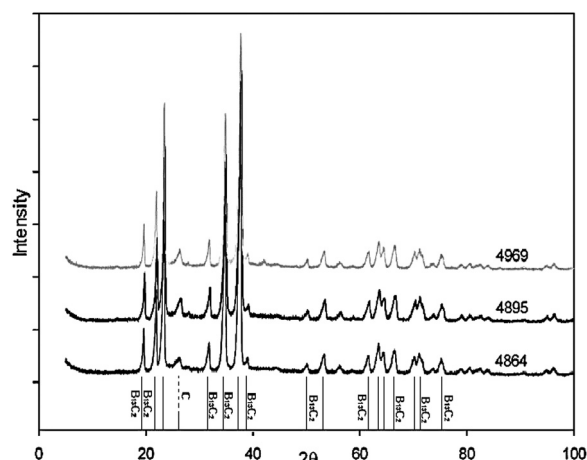


Fig. 1. XRD pattern of 4969 (top), 4895 (middle) and 4864 (bottom) for as received powders. Peaks are identified as a solid line for B_4C and a dotted line for free carbon.

present as graphite due to the high temperatures at which B_4C powder is produced, is generally present at some level in B_4C powders as it is preferable to have excess carbon than excess oxide left over from the production process whereby boron anhydride (B_2O_3) is reduced using carbon [1]. A minor disturbance of the signal at $28.2^\circ 2\theta$, which is the prominent peak for boric acid, could be interpreted as evidence of oxide but the lack of a peak at $15.5^\circ 2\theta$, the secondary peak, indicates that oxide levels are too low for quantitative data to be extracted from the pattern. In reality, the general consensus is that there is most likely a thin layer of oxide present on the surface of the powders [10,25–27]. LECO analysis shown in Table 1 shows that there is oxygen present in some form within the powder but it is impossible to say what form this is present in.

Fig. 2 shows the thermogravimetric analysis (TGA) and differential scanning calorimetry data for the as-received powders in a nitrogen atmosphere. TGA data shows evidence that the powders may have temperature sensitive contaminants within them, particularly below 500°C . Initially, from 20°C to 120°C the large majority of mass loss will consist of adsorbed water, the continued mass loss beyond this temperature up to 450°C can be attributed to the dehydration of H_3BO_3 to produce steam [28]. The adsorbed water levels are 0.35%, 0.13% and

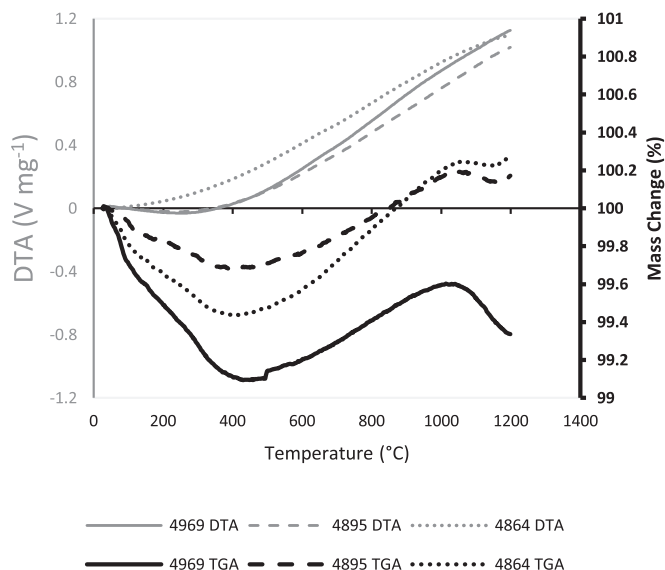


Fig. 2. TGA and DSC data for as-received powders.

Table 2
Particle size data for three HD7 powders.

	4969	4864	4895
Particle size			
$d_{10} (\mu\text{m})$	0.47	0.58	0.53
$d_{50} (\mu\text{m})$	1.64	2.2	2.1
$d_{90} (\mu\text{m})$	4.57	5.4	6.1
SA ($\text{m}^2 \text{ g}^{-1}$)	10.3 ± 0.1	7.9 ± 0.1	8.3 ± 0.1
O (at%)	0.887 ± 0.08	0.593 ± 0.05	0.692 ± 0.08
N (at%)	0.285 ± 0.01	0.167 ± 0.01	0.170 ± 0.01

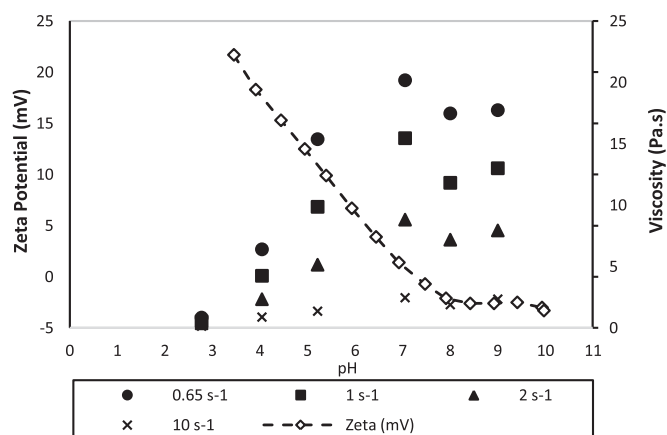


Fig. 3. Effect of pH on ζ -potential (15 vol%) and viscosity (30 vol%) of HD7 4969 B₄C suspension.

0.23% for powders 4969, 4895 and 4864 respectively. The total loss up to 450 °C is 0.90%, 0.31% and 0.55% for powders 4969, 4895 and 4864 respectively. It can be argued that the increased mass loss for 4969 relative to the other two powders comes from its larger surface area, by default increasing the water loss from the two mechanisms. Above 450 °C, which corresponds to the oxidation of B₄C, mass gain is observed. It is proposed that this is due to trace quantities of oxygen in the purge stream causing oxidation of the powder. The data appears to suggest that there is a shift in dominant mass transfer mechanism at 1050 °C, though it is impossible to determine what this is without further analysis. The DSC trace shows that with increasing temperature more heat is required which is indicative of oxidation. On the basis of this evidence, it is fair to assume that, although very slight differences are present, that thermal analysis does not reveal anything that would suggest these powders would perform differently when added to water. If contaminants were to be identified then thermal analysis can be tailored to look at any points of interest.

3.2. Effect of pH on zeta potential and rheology of as-received powder suspensions

[3,4] and 5 show the ζ -potential for three B₄C powders at 0.15 ϕ alongside the same suspension at 0.3 ϕ . Considering the ζ -potential, it is evident that there were significant differences in behaviour between the powders, which must be considered if the powder is to be processed

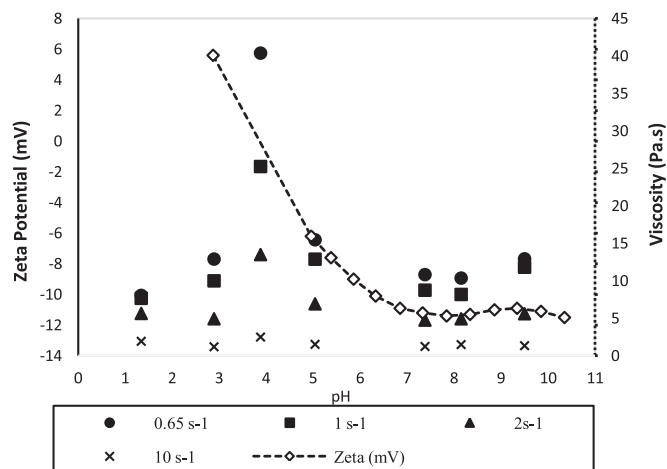


Fig. 4. Effect of pH on ζ -potential (15 vol%) and viscosity (30 vol%) of HD7 4864 B₄C suspension.

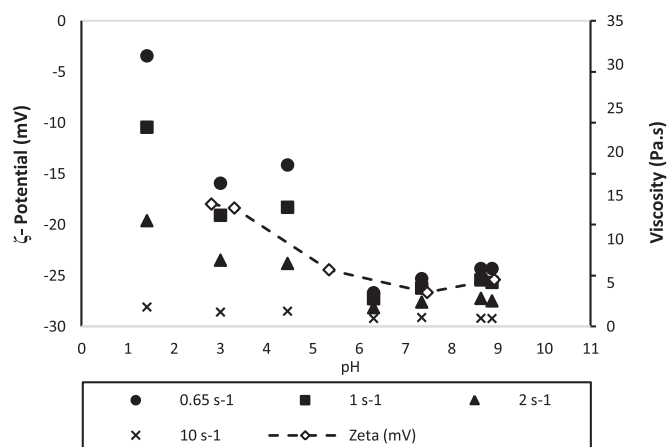


Fig. 5. Effect of pH on ζ -potential (15 vol%) and viscosity (30 vol%) of HD7 4895 B₄C suspension.

aqueously.

Fig. 2 suggests that 4969 B₄C has a low ζ -potential under basic conditions and only has the potential to be stabilised in moderately acidic regions (< pH 4). However this was not confirmed in this study as the test was only conducted to a minimum pH of 4. The IEP for this suspension occurred at pH 7.

Contrasting to this, Fig. 4 suggests that 4864 B₄C suspension has a very low ζ -potential throughout the pH range tested, suggesting that stabilisation cannot be achieved purely through electrostatic means and a dispersant would be necessary to achieve sufficient stabilisation. The IEP for this suspension occurred at pH 4.

For the third suspension tested (batch 4895), Fig. 5 suggests that the ζ -potential remains significantly negative across all the pH values tested. Although an IEP was not observed, it is probable that it would occur below pH 2. This data suggests that there is something fundamentally different between the three powders that means stabilisation through purely electrostatic mechanisms requires three different approaches. It is likely that the B₄C powders have different surface properties, such as residual dispersants, which is contributing to this behaviour.

It is also worth noting that all the powders, when added to deionised water, produced an acidic slurry with a pH of less than 2. This means that on addition to water that only 4969 powder (Fig. 3) is operating well away from the IEP at moderate ζ -potential levels. In the case of 4895 (Fig. 5), addition to water with no adjustment results in the slurry operating at its IEP and significant agglomeration will occur. This means it may be more energy efficient to adjust the pH of the water before the addition of the powder.

Considering the viscosity of the suspensions, it can be concluded that the ζ -potential of B₄C powders has the expected effect with lower absolute ζ values resulting in higher viscosities. Of particular note, it can be said that the IEP of all the suspensions correlates to the highest viscosity for all suspensions tested. Previously there was concern that the semiconducting nature of B₄C would influence the measurements but it is clear that such effects were negligible within the scope of these trials. The effect of the dielectric constant between the values stated for B₄C (4.8–8.0) was found to be negligible. This validates that electro-acoustic spectroscopy can be used to effectively determine the ζ -potential of B₄C suspensions so long as sufficient flow is retained.

The solids concentration of the suspension appeared to have no bearing on the ζ -potential measurements above 15 vol%. However practically, issues were observed in higher concentration suspensions (i.e. 30 vol%) close to the IEP. Titration through the IEP had the potential to cause the enhanced attenuation cell to clog with suspension. This inevitably produced unusual results and the cell had to be cleared

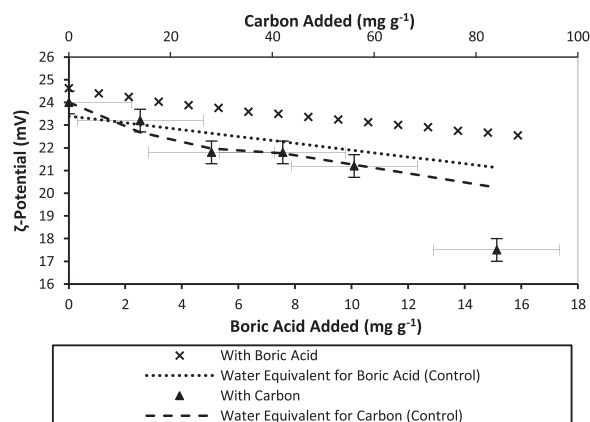


Fig. 6. Effect of boric acid and carbon additions on the ζ -potential of 4969 B₄C powder.

before valid results could be obtained again.

3.3. Effect of boric acid and free carbon content on zeta potential

As identified in Section 3.1, the powders all show evidence that oxide and free carbon are present in some form. Fig. 6 shows the effect that boric acid and carbon additions have on the ζ -potential of 4969 powder. Note that in order to achieve sufficient dispersion both additives were added in a solution of water of 4 wt% and 10 wt% for boric acid and carbon respectively. To determine any dilution effects, a control experiment was set up whereby deionised water was added to the system. These are shown by the broken lines in Fig. 6 and correspond to the water equivalent of the associated solution, these purely act as a reference and do not correspond to the x-axis values as written. In actuality, 1 mg g⁻¹ carbon is the equivalent to having added 0.34 ml of water to the system; and 1 mg g⁻¹ boric acid is the equivalent of having added 0.944 ml of deionised water. It is also worth noting that the pH of the boric acid doped system from 0 mg g⁻¹ to 16 mg g⁻¹ rose from 2.95 to 3.03. The carbon system increased from 2.95 to 3.26 up to 84 mg g⁻¹.

From Fig. 6 it is evident that dilution of the slurry results in a reduction in the ζ -potential. This reduction can be attributed to the slight increase in pH which reduces the ionic strength. This means that the potential across the electrical double layer (EDL) does not diminish as quickly, as the charged surface becomes less shielded due to the reduction in ion concentration, and the Debye length (κ) becomes thicker.

With this observation, it is possible to say that boric acid concentration has minimal effect on the ζ -potential under acidic conditions. Basic conditions were not investigated in this study, as Hawn and Williams (1991) have already shown that at pH values above 8 the presence of boric acid induces electrostatic shielding phenomenon. This would be expected as H₃BO₃, acting as a Lewis acid, dissociates to become H₃BO₄⁻ which bonds to the positive ion of any bases present, thus shielding the surface charge.

3.4. Effect of dispersant concentration on zeta potential

Figs. 7, 8 and 9 demonstrate the affect that an anionic dispersant had on three B₄C powders in water. Dispex caused the ζ -potential to become more negative with increasing concentration and had a much more significant effect at lower concentrations. This is most likely due to the colloid surface becoming saturated with dispersant and excess dispersant going into the suspending medium. Subsequent additions of dispersant caused the conductivity of the suspending medium to increase. Along with this, a pH shift towards the natural pH of Dispex (pH = 8) occurred, a condition at which the dispersant is most effective. This kind of behaviour is considered standard in anionic dispersants.

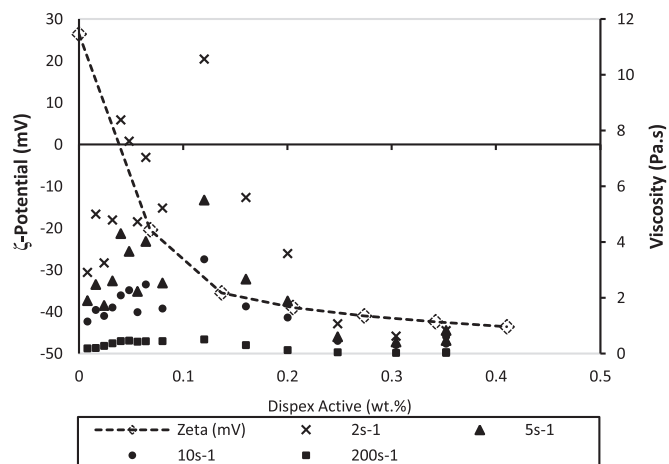


Fig. 7. Effect of Dispex® concentration on ζ -potential (15 vol%) and viscosity (30 vol%) of HD7 4969 B₄C suspension.

Comparing the individual suspensions, it appears that the point at which excess additions resulted in a lower ζ -potential decrease was related to the initial ζ -potential of the suspension. Considering ζ -potential only, suspension 4969 (Fig. 7) with a starting ζ -potential of approximately +27 mV requires 0.12 wt% of Dispex agent. Suspensions 4864 (Fig. 8) and 4895 (Fig. 9) with a starting ζ -potential of around -7 mV and 14 mV required approximately 0.1 wt% and 0.075 wt% respectively. It was observed that the anionic dispersant had the ability to increase the magnitude of ζ -potential above 25 mV in all three of the suspensions. Any instability in the suspension beyond this point is unlikely to be related to ζ -potential.

In terms of viscosity, it appears that the start of the plateauing region of the ζ -potential underestimates the amount of dispersant needed. For 4969, optimum viscosity was observed at a dispersant concentration of 0.3 wt% which corresponds to 0.18 wt% more Dispex than predicted by the ζ -potential. Interestingly, the viscosity at total surface coverage (0.125 wt%) is at its highest for 4969 even with a ζ -potential of -30 mV. This could be explained by the amount of variability occurring at low dispersant concentrations and the viscosity of this suspension being significantly higher than the other two suspensions. It is important to note that initially the viscosity of the 4969 suspension rises with an increase in dispersant levels before dropping, as would be predicted by the ζ -potential measurements made via electroacoustic spectroscopy.

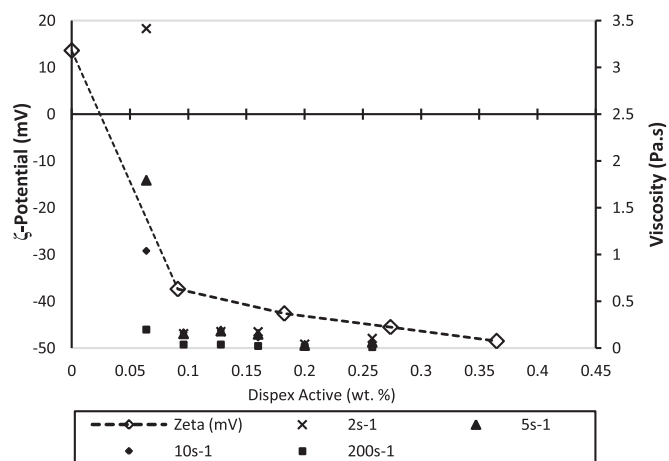


Fig. 8. Effect of Dispex® concentration on ζ -potential (15 vol%) and viscosity (30 vol%) of HD7 4864 B₄C suspension.

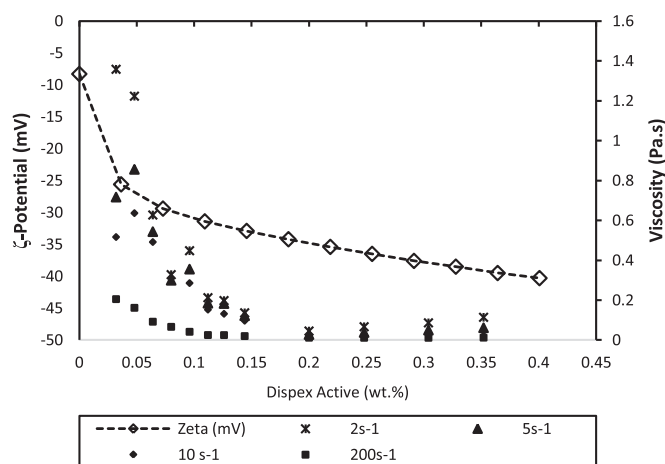


Fig. 9. Effect of Displex® concentration on ζ -potential (15 vol%) and viscosity (30 vol%) of HD7 4895 B₄C suspension.

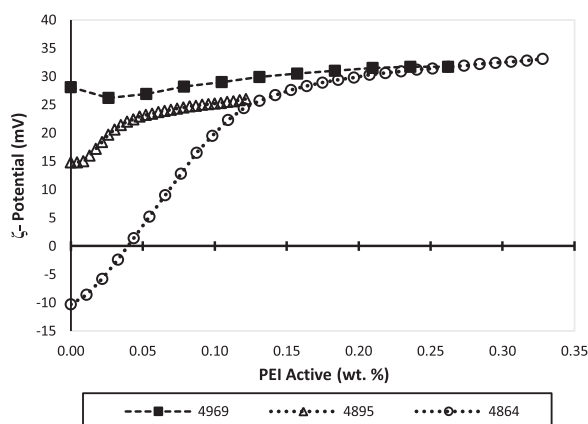


Fig. 10. Effect of polyethylenamine M.W. 50,000–100,000 concentration on ζ -potential of three B₄C suspensions starting at natural pH (< pH 2.5).

PEI behaves in a similar fashion but with the charge sign reversed as would be expected by a cationic adsorbent, as shown in Fig. 10. It appears as though the maximum obtainable ζ -potential, with a ζ_{\max} of about +30 mV, is slightly lower magnitude than that of Displex with a ζ_{\max} of between -40 mV and -50 mV. Interestingly, suspension 4864 appears to level out at a lower magnitude ζ -potential for PEI than the other two suspensions but levelled out higher than the other two when Displex is used. From an electrostatic stability perspective, it appears as though Displex is more effective at dispersing B₄C suspensions however it was worth noting that steric mechanisms are not accounted for which could prove otherwise. Dispersants can be used to effectively mask any differences in ζ -potential between different B₄C batches, yet it is clear from these experiments that the ζ -potential should not be a sole indicator for suspension stability.

Another factor that may be influencing the behaviour of the powders in water is the carbon content within the batches. From XRD in Fig. 1, it is evident that there is a peak between 24 and 26.6 two theta, indicating that there is carbon of various degrees of graphitisation present in the powder [29]. It is also possible that there was amorphous carbon present which was not observed. It may be more appropriate to treat the system as one with two different particles, and therefore ζ -potentials. For this to be done it would be necessary to calculate the concentration of free carbon within the powder. The relevant information could then be fed back into the Acoustosizer and its software to determine the charge surrounding each type of particle.

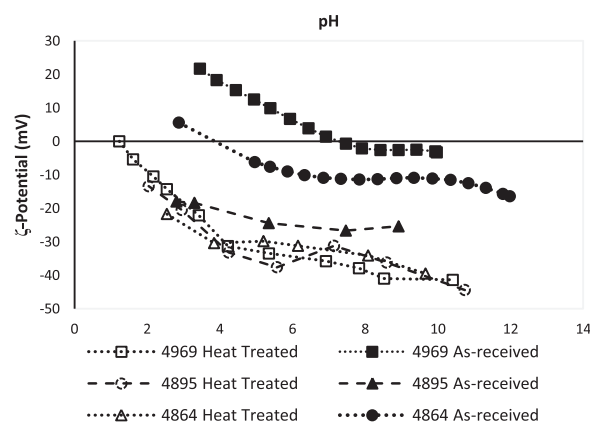


Fig. 11. Comparison of ζ -potential between heat treated (unfilled markers) and as-received (filled markers) B₄C suspensions.

3.5. Effect of pH on zeta potential of heat-treated powder suspensions

After validation of the electroacoustic spectroscopy in Section 3.2 and the subsequent discussion of the effect of dispersants, oxide and carbon content, the ζ -potential of heat-treated powders can be discussed more thoroughly. Fig. 11 presents the ζ -potential of powders heat-treated in argon at 450 °C for 60 mins (heating rate 0.33 C min⁻¹) alongside the as-received data for comparison. The purpose of this was to breakdown any residual polymers (i.e. dispersants) on the surface and reveal the ζ -potential of an uncontaminated B₄C surface.

Looking at Fig. 11, heat-treated powders have their ζ -potential is shifted to more negative values across all pH values. This puts forward evidence that there is likely a charged surface species of cationic nature on the powders at varying degrees of concentration. It was also observed that the natural pH of these slurries was between 3.5 and 4.5, making them considerably less acidic than their as-received counterparts. It is proposed that increasing levels of contamination are present from 4895 through to 4969, to the point that the maximum obtainable basic ζ -potential is restricted. Heat-treating the powder enables the negatively charged surface of B₄C to stabilise the suspension electrostatically above pH 4 and the IEP of all the powders to occur below pH 2.5. This results in the powders performing consistently across batches and away from the IEP without the need for pH adjustment.

4. Conclusions

Electroacoustic spectroscopy has been used to determine the ζ -potential of high solids loading (15 vol%) B₄C suspensions across the pH range. The viscosity of the suspensions at each pH were shown to correlate with the ζ -potential magnitude, as expected, with the highest viscosity being observed at the IEP in each case. These observations provide confidence in the validity of electroacoustic spectroscopy for determining ζ -potential of B₄C particles in water. The work has also shown that B₄C powder can vary quite significantly from batch to batch once in suspension, despite nominally being of the same specification. Heat treatment of powders can normalise powders in terms of their ζ -potential, indicating that there is likely small quantities of contamination present on as received powders. Electroacoustic characterisation is a useful tool in providing information on B₄C powder and may be of particular use to manufacturers looking to screen powders.

It was also found that dispersant must be added in concentrations greater than where the maximum ζ -potential is observed to obtain the lowest viscosity. This is put down to the steric hindrance effect of the dispersants still having a role to play once electrostatic repulsion has been maximised.

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